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三台花中的一新奇化合物——Serratumin A*

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摘要：从云南西双版纳产的三台花（*Clerodendrum serratum* var. *amplexifolium* Moldenke）的地上部分分离到 6 个化合物，它们的结构通过波谱解析（包括 2D NMR 技术）得到鉴定. 其中化合物 1 是一新奇的单萜烯酸和单糖衍生物的缩合物，命名为 serratumin A（1）；化合物 2～6 为首次从该植物中分离得到。

关键词：三台花；马鞭草科；缩合物；Serratumin A
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Serratumin A, a Novel Compound from *Clerodendrum serratum* *

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Abstract: Phytochemical investigation of the plant *Clerodendrum serratum* var. *amplexifolium* Moldenke afford a novel condensation compound of a monoterpene acid with a monosaccharide derivative, named serratumin A (1), and five known compounds (2～6) which have been isolated from the plant source for the first time. Their structures were characterized by spectral methods (including 2D NMR technique).

Key words: *Clerodendrum serratum* var. *amplexifolium*; Verbenaceae; Condensation compound; Serratumin A

Clerodendrum serratum var. *amplexifolium* Modenke (Verbenaceae) is wildly distributed in the southern region of Yunnan Province and South－western region of Guizhou Province, China. It mainly grows in the place up to an altitude of 630 ～ 1 700 meters (Wu *et al*, 1977). It is a famous folk herbal medicine called" San Tai Hua "(三台花) in traditional Chinese medicine and has a good reputation in the treatment of various human disorders such as the malaria, hepatitis, bullas pustulosis and various infections (Wu *et al*, 1977; Yunnan Medicinal Material Corporation, 1993). However, its chemical constituents have not been reported so far. In order to clarify the medical value of the plant, and as a series of study on

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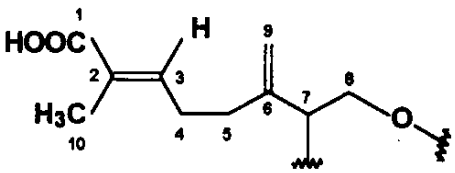
biologically active constituents of the genus *Clerodendrum*, this medicinal plant was investigated.

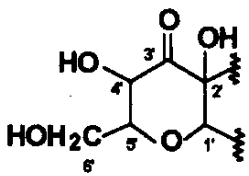
The study of the plant led to the isolation of a new compound, named serratumin A (1), together with five known compounds including two flavonoids, 5,7,8,4'-tetrahydroxy-6-methoxy-flavone (2) (Wang *et al*, 1998) and 5,6,7-trihydroxy-4'-methoxyflavone 7-glucopyranoside (3) (Morita *et al*, 1977); and three phenolic acids, *cis*-cinnamic acid (4), *trans*-cinnamic acid (5) (Hocking *et al*, 1970) and *p*-coumaric acid (6) (Tsareva *et al*, 1971). Their structures were elucidated by spectroscopic methods (including 2 D NMR techniques).

Results and Discussion

Serratumin A (1) exhibited an $[M+1]^+$ ion peak at m/z 343 in the positive FABMS and an $[M-H_2O]^+$ ion peak at m/z 324 in the EIMS indicating its molecular weight to be 342. The molecular formula was determined as $C_{16}H_{22}O_8$ by the high resolution positive FABMS ($[M+1]^+$ 343.1402, calcd. 343.1393). The ^{13}C NMR spectrum showed 16 resonance signals (Table 1), providing further support for the assigned molecular formula. Observation of the ^{13}C NMR resonance for four olefinic carbons [δ 114.9(t), 129.8(s), 140.9(d) and 141.9 (s) ppm] and two carbonyl carbons [δ 170.5(s) and 209.6(s) ppm] accounted for a total of 4 degrees of unsaturation. The remaining 2degrees of unsaturation were assumed for the presence of two additional ring systems. The IR spectrum displayed the existence of hydroxyl groups (3418 br. cm^{-1}), a carboxyl group (1704 cm^{-1}) of an α, β- unsaturated acid, a carbonyl group (1642 cm^{-1}) and olefinic bonds (3020, 1425 and 682 cm^{-1}). The ^1H NMR spectrum of 1 was performed in C_5D_5N to give an excellent results as shown in Table 1. By investigating the ^1H and ^{13}C NMR spectra as well as $^1H-^1H$ COSY, HMQC and HMBC spectra (Table 2) of 1, two partial structures, (a) and (b) (Fig.1), were predicated. The structure of (a) was determined to be a monoterpene acid; and (b) was suggested to be a derivative of a hexose, i.e



(a)



(b)

Fig. 1 Two partial structures, (a) and (b)

the -OH at C-3'of the hexose was oxidated to carbonyl group. It was confirmed by the presence of a downfield signal [δ 5.37(1H, d, J = 10.0 Hz, H-4')] in ^1H NMR spectrum of 1, since the H-4' is highly deshielded by the carbonyl group at C-3'. Now the remaining question is how to connect each other of the two partial structures. On the basis of the

unsaturated degree, the connectivity of the two partial structures should give an additional ring system. From the HMBC spectrum of 1, some important $^{1}H-^{13}C$ long range correlations could be clearly observed between H－7 (δ 3.86 ppm) of (a) and C－1′ (δ 110.4 ppm), C－2′(δ 87.38 ppm) and C－3′(δ 209.6 ppm) of (b), respectively; between H－8(δ 4.54 ppm) of (a) and C－1′(δ 110.4 ppm), C－2′(δ 87.38 ppm) of (b), respectively; between H－1′(δ 5.55 ppm) of (b) and C－7(δ 51.80 ppm), C－8(δ 71.96 ppm) of (a), respectively. These evidence revealed that the two partial structures were combined by a carbon－carbon bond between C－7 and C－2′, and an oxo－bridge between C－8 and C－1′. Meanwhile, a new tetrahydrofuran circle was formed. On the other hand, the configuration of $\Delta^{2,3}$－double bond and relative stereochemistry of 1 was determined by the NOESY experiments (Table 2). Accordingly, the structure of serratumin A was identified as 1. Its structure was shown in Fig. 2.

The structures of five known compounds were identified on the basis of physical constants and spectral data.

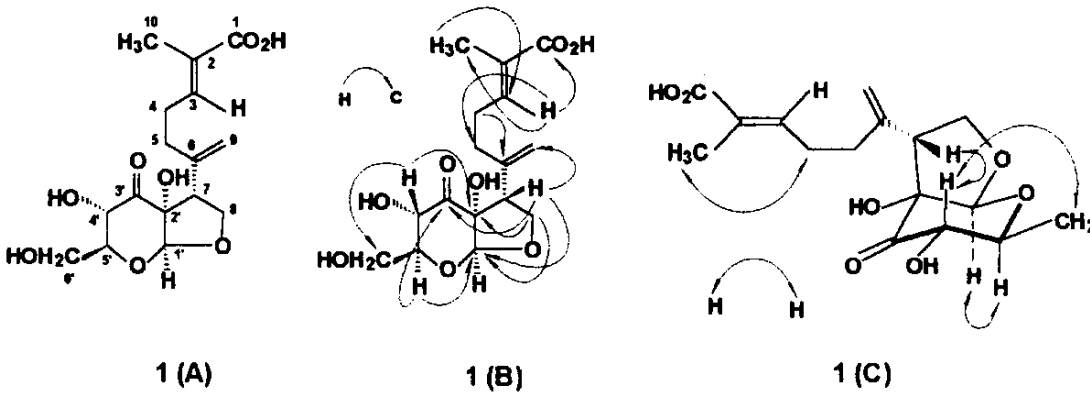


Fig.2 (A): The structure of 1 (B): The key $^{1}H-^{13}C$ long－range correlations observed in the HMBC spectrum of 1. (C): Some principal results observed in the NOESY spectra of 1.

Table 1　The ^{1}H and ^{13}C NMR spectra data of compounds 1 in pyridine－d_5 (500MHz, δ in ppm from TMS and J in Hz)

H／C	δ_H	δ_C
1		170.5 s
2		129.8 s
3	6.93(1H, br.d, J = 5.8)	140.9 d
4	2.19(2H, m)	27.40 t
5	2.19(2H, m)	35.44 t
6		141.9 s
7(7β)	3.86(1H, t, J = 9.2)	51.80 d
8	4.54(2H, m)	71.96 t
9(9a, 9b)	5.02(1H, br.s); 5.14(1H, br.s)	114.9 t
10	1.91(3H, s)	12.95 q
1′(1′α)	5.55(1H, s)	110.4 d
2′		87.38 s
3′		209.6 s
4′(4′β)	5.37(1H, d, J = 10.0)	72.58 d
5′(5′α)	3.92 (1H, dt, J = 10.0, 1.8)	78.74 d
6′	4.46(2H, br.s)	62.27 t

Table 2 Some principal results from the $^1H - ^1H$ COSY, NOESY and HMBC spectra of compound 1 in pyridine－d_5(500MHz)

Proton	COSY(^1H)	NOESY(^1H)	HMBC * (^{13}C)
3	4	4, 5	1, (4), 5, 10
4	3, 5	3, 5, 10	2, (3), (5), 6
5	4	3, 7β, 9a	3, (4), (6), 7, 9
7β	8	5, 8, 4′β	5,(6),(8), 9, 1′,(2′), 3′
8	7β	7β, 9b	6, (7), 1′, 2′
9a	9b	5	5, (6), 7
9b	9a	8	5, (6), 7
10		4	1, (2), 3
1′α		5′α	7, 8, (2′)
4′β	5′α	7β, 6′	2′, (3′), (5′), 6′
5′α	4′β, 6′	1′α, 6′	1′, 3′
6′	5′α	4′β, 5′α	4′, (5′)

* Two－bond correlations were shown in the brackets.

Experimental

General Optical rotations were taken on JASCO－20C digital polarimeter. IR spectra were recorded with Bio－Rad FTS－35 spectrometer. UV spectra were obtained on a UV210A spectrometer. MS spectra were measured on a VG Auto Spec － 3000 spectromet－er. NMR spectra were run on a Bruker AM－400 MHz and DRX－500 MHz spectrometers.

Extraction and Isolation Plant material was collected in Xishuangbanna of Yunnan province in september 1996, and identified as *C. serratum* var. *amplexifolium* by Prof. Li Xi－wen. A voucher specimen is deposited in the Herbarium of Kunming Institute of Botany. The air－dried and powdered aerial parts (6.0 kg) of C. *serratum* var. *amplexifolium* were extracted with 95% EtOH (3×16 L) under reflux for 2 hr. each time and then concentrated in vaccum to give blackish green sticky crude extract (628.2 g). The extract was dissolved in H_2O and successively partitionated with petroleum－ether (60 ～ 90 ℃), EtOAc and n－BuOH to affored petroleum－ ether, EtOAc and n－BuOH residues 120.5, 57.0 and 256.0 g after the solvent was evaperated to dryness in vaccum, respectively.

The EtOAc residue (57.0 g) was chromatographed on silica gel column (1.5 kg, 200～300 mesh) and eluted with $CHCl_3$／Me_2CO gradient system (1∶0 － 0∶1) and then with MeOH to give twelve fractions (**A**～**L**), respectively. From the fractions **D** and **E**, compounds **4**(150 mg), **5**(1.049 g) and **6**(1.186 g) were isolated by CC on silica gel (300～400 mesh) eluting with petroleum－ether／$CHCl_3$(9∶1), petroleum－ether／Me_2CO (10∶1) and petroleum－ether／Et_2O (2∶9), respectively. Fractions **G** and **H** were chromatographed on medium pressure column developing with petroleum－ether／Et_2O (4∶6), $CHCl_3$／MeOH (90∶1 and 10∶1) and Et_2O to yield compounds **1** (82 mg) and **2** (26 mg). After repeated silica gel and reversed phase material RP－8, RP－18 and MCI gel CHP－20 [eluent∶$CHCl_3$／MeOH (9∶2 and 8∶2), $CHCl_3$／MeOH／H_2O (9∶1∶0.1 and 8∶2∶0.2), MeOH／H_2O (3∶7, 4∶6 and 5∶5)] CC and increasing pressure CC, compound 3 (31 mg) was obtained from fraction **J**.

Serratumin A (1) $C_{16}H_{22}O_8$, brown gum, $[\alpha]_D^{16.7}$ + 11.53°(c 0.009, C_5H_5N), UVλ_{max}^{MeOH} nm: 202, 214.5, 253.5 and 258.5; IRν_{max}^{KBr} cm^{-1}: 3418 br., 3020, 2936, 1704, 1642, 1488, 1425, 1385, 1248, 1086, 755 and 682; EIMS (70 eV, m/z (%)): 324$[M - H_2O]^+$ (20), 306$[324 - H_2O]^+$ (24), 294 (15), 264 (16), 235 (17), 217 (20), 206 (30), 193 (22), 177 (54), 166 (62), 148 (62), 121 (100) and 107 (58); positive ion FABMS m/z: 343 $[M + 1]^+$ (100); Its ^1H and ^{13}C NMR spectral data were listed in Table 1.

5, 7, 8, 4′ - tetrahydroxy - 6 - methoxyflavone (2) $C_{16}H_{12}O_7$, red-orange crystal, mp: 162～164°C; IRν_{max}^{KBr} cm^{-1}: 3360(br.), 3122, 1650, 1580, 1562, 1494, 1430, 1392, 1213, 1168, 1086, 1055 and 955; ^1H NMR (400 MHz, DMSO): δ 6.54(1H, s, H-3), 7.40(2H, dd, J = 8.4, 2.0 Hz, H-2′ and 6′), 6.87(2H, dd, J = 8.4, 2.0 Hz, H-3′ and 5′), 3.90(s, OCH3) and 12.95(1H, s, 5-OH); ^{13}C NMR (100.6 MHz, DMSO): δ164.1(s, C-2), 102.4(d, C-3), 182.0(s, C-4), 149.7(s, C-5), 131.4(s, C-6), 152.8(s, C-7), 128.6(s, C-8), 145.7(s, C-9), 103.7(s, C-10), 59.53(q, 6-OCH_3), 121.6(s, C-1′), 128.9(d, C-2′ and 6′), 116.0(d, C-3′ and 5′) and 161.5 (s, C-4′); EIMS(70 eV) m/z: 316$[M]^+$ (59), 301$[M-Me]^+$ (45), 273(36), 197(43), 183$[A_1 - Me]^+$ (10), 167(34), 155(29) and 118$[B_1]^+$ (27).

5,6,7 - trihydroxy - 4′ - methoxyflavone - 7 - O - (- D - glucopyranoside (3) $C_{22}H_{22}O_{11}$, amorphous yellow powder, $[\alpha]_D^{22}$ - 63.78° (c 0.780, C_5H_5N); UVλ_{max}^{MeOH} nm: 203, 211, 255.5, 260, 277 and 332; IRν_{max}^{KBr} cm^{-1}: 3394(br.), 2931, 1660, 1606, 1570, 1512, 1464, 1357, 1286, 1252, 1180, 1101, 1073, 1036, 915 and 836; ^1H NMR (400 MHz, C_5D_5N): δ6.54(1H, s, H-3), 7.57(1H, s, H-8), 7.87(2H, br.d, J = 7.6 Hz, H-2′ and 6′), 6.87(2H, br.d, J = 7.6 Hz, H-3′ and 5′), 5.92(1H, d, J = 7.0 Hz, H-1″), 4.00 (1H, t, J = 7.4 Hz, H-2″), 4.34(2H, m, H-3″and 4″), 3.78(1H, m, H-5″), 4.56 (1H, dd, J = 11.5, 2.0 Hz, H-6a″), 4.39(1H, dd, J = 11.5, 5.3 Hz, H-6b″) and 4.05(s, 4′-OCH_3); ^{13}C NMR (100.6 MHz, C_5D_5N): δ157.6(s, C-2), 103.6(d, C-3), 184.3(s, C-4), 153.2(s, C-5), 134.0(s, C-6), 165.2(s, C-7), 95.26(d, C-8), 154.1(s, C-9), 107.1(s, C-10), 122.1(s, C-1′), 129.1(d, C-2′ and 6′), 117.1(d, C-3′ and 5′), 163.1(s, C-4′), 60.50(q, 4′-OCH_3), 102.2(d, C_{glc}-1), 74.88(d, C_{glc}-2), 79.39(d, C_{glc}-3), 71.36(d, C_{glc}-4), 78.68(d, C_{glc}-5) and 62.58(t, C_{glc}-6); negative ion FABMS (m/z): 461$[M - 1]^-$ (100), 299$[M - Glc]^-$ (64), 283 (24), 255(31), 189(35), 117(6) and 80(10).

Cis-cinnamic acid (4) $C_9H_8O_2$, white powder, UVλ_{max}^{MeOH} nm: 204.5, 206.5, 214.5, 219 and 268. IRν_{max}^{KBr} cm^{-1}: 2931, 1695, 1631, 1451, 1419, 1311, 1283, 1223, 1176, 1028, 980 and 943; ^1H NMR (400 MHz, $CDCl_3$): δ 7.58(2H, dd, J = 6.6, 2.6 Hz, H-2 and 6), 7.34(3H, m, H-3, 4 and 5), 5.96(1H, d, J = 12.7 Hz, H-β) and 7.04(1H, d, J = 12.7Hz, H- γ); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ134.1(s, C-1), 128.0(d, C-2 and 6), 129.3(d, C-3 and 5), 130.1(d, C-4), 172.1(s, C-α), 118.9(d, C-β)

and 145.4(d, C－γ); EIMS(70 eV) m/z: 148[M]$^+$(100), 131[M－OH]$^+$(27), 120[M－CO]$^+$(12), 103[M－ COOH]$^+$(73), 91(26) and 77(42).

Trans－cinnamic acid (5) $C_9H_8O_2$, colorless crystal, $[\alpha]_D^{16.0}$ + 0.34° (c 1.480, $CHCl_3$); UVλ_{max}^{MeOH} nm: 204.5, 208, 214.5, 220.5 and 269.5. IRν_{max}^{KBr} cm^{-1}: 3067, 3028, 2834, 1683, 1629, 1449, 1421, 1335, 1314, 1285, 1222, 980 and 944; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54(2H, dd, J = 5.6, 2.0 Hz, H－2 and 6), 7.40(3H, m, H－3, 4 and 5), 6.45(1H, d, J = 16.0 Hz, H－β) and 7.79(1H, d, J = 16.0 Hz, H－γ); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 134.0(s, C－1), 128.3(d, C－2 and 6), 128.9(d, C－3 and 5), 130.7(d, C－4), 172.5(s, C－α) and 117.3(d, C－β), 147.0(d, C－γ); EIMS(70 eV) m/z: 148[M]$^+$(100), 131[M － OH]$^+$(27),120[M － CO]$^+$(12), 103[M － COOH]$^+$(73), 91(26) and 77(42).

P－coumaric acid (6) $C_9H_8O_3$, colorless crystal, $[\alpha]_D^{16.0}$ + 0.93°(c 0.810, H_3COH); UVλ_{max}^{MeOH} nm: 210, 225, 292, 298.5 and 308.5. IRν_{max}^{KBr} cm^{-1}: 3376, 2831, 2501, 1673, 1628, 1600, 1511, 1449, 1326, 1314, 1246, 1214, 1172 and 979; ^{1}H NMR (400 MHz, CD_3OD): δ 7.41(2H, dd, J = 8.6, 1.4 Hz, H－2 and 6), 6.79(2H, dd, J = 8.6, 1.4 Hz, H－3 and 5), 6.26(1H, d, J = 15.9 Hz, H－β) and 7.60(1H, d, J = 15.9 Hz, H－γ); ^{13}C NMR (100.6 MHz, CD_3OD): δ127.2(s, C－1), 131.0(d, C－2 and 6), 116.8(d, C－3 and 5), 161.0(s, C－4), 171.1(s, C－α), 115.5(d, C－β) and 146.7(d, C－γ); EIMS (70 eV) m/z: 164[M]$^+$(69), 147(69),136(38), 122(69), 108(100), 101(33), 94(46), 90(57), 78(70), 62(66) and 53(67).

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